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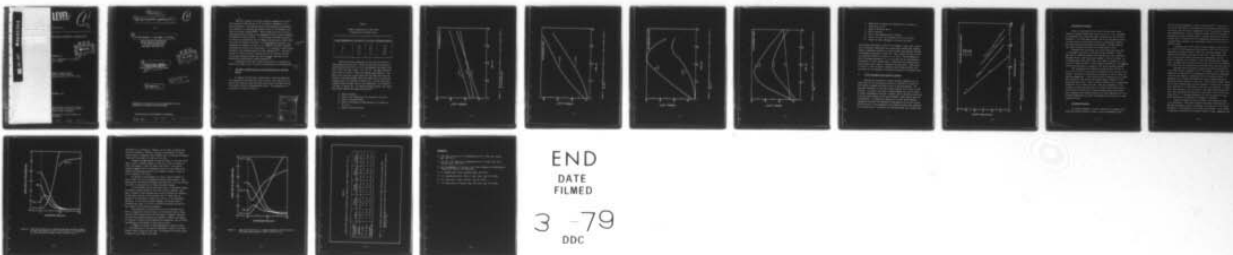
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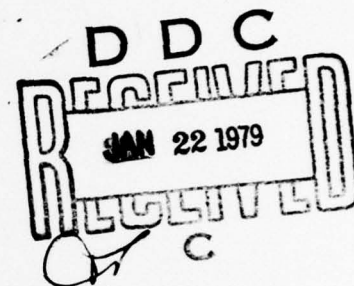
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THE DELAYED FRACTURE OF ALUMINUM ALLOYS



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Our prior studies on the grain boundary segregation of Al-Zn-Mg alloys have shown that Mg and Zn are heavily segregated to the grain boundaries. AES studies coupled with plasmon-loss measurements have enabled us to identify the chemical state of the segregants present on the grain boundary<sup>(1,2)</sup>. These studies show that in the as-quenched condition, the Mg and Zn segregated along the grain boundaries are present in solid solution. In the peak-and over-aged conditions, all the Zn is incorporated into the  $MgZn_2$  particles while a major fraction of Mg is present as free Mg. In the as-quenched condition, the segregants are confined to about 50 to 100 <sup>ANGSTROM</sup>  $\text{\AA}$  from the grain boundary. Utilizing the vacancy solute drag model, it is possible to qualitatively account for the observed extent of solute segregation<sup>(3)</sup>. The implications to stress corrosion cracking (SCC) of the free Mg observed on the grain boundaries under all heat treatment conditions can be analyzed by proposing Mg-H complex formation<sup>(4)</sup>.

Consequently this year's efforts were focused on studying the effect of the Mg/Zn ratio on the SCC susceptibility of Al-Zn-Mg alloys.

A. The Effect of Mg/Zn Ratio on SCC Susceptibility of Al-Zn-Mg Alloys

To analyze the influence of Mg/Zn ratio on SCC susceptibility four high purity Al-Zn-Mg alloys were produced. The alloy pairs A,B and C,D were chosen so that each pair would contain the same total Mg + Zn content but with different Mg/Zn ratios. The compositions of the alloys are listed in Table I.

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TABLE I.

Chemical Composition of New Series  
of High-Purity Al-Zn-Mg Alloys

Alloy Designation	Mg (wt.%)	Zn (wt.%)	Total Mg and Zn
A	2.5	5.3	7.8
B	3.7	4.4	8.1
C	2.6	7.7	10.3
D	4.0	6.4	10.4

These alloys were homogenized and hot and cold rolled to a final gauge of about 0.040". Strips of these alloys were given a solution anneal at 475°C for 2 hr, water-quenched, and aged at RT, 90°C, 150°C, and 180°C (Figs. 1,2,3, and 4). The aging curves for alloy pairs A, B and C, D show very similar aging behavior. The goal of the study was to age alloys with the same total Mg and Zn content to the same hardness level and conduct tests to study SCC susceptibility as a function of Mg/Zn ratio. All the tests were conducted under constant load at room temperature in a solution of 3.5% NaCl at neutral pH. To eliminate surface effects, the following surface cleaning procedure was adopted<sup>(4)</sup>:

1. Wash in acetone.
2. Pickle in 50 g HNO<sub>3</sub>/liter for one hour at 30 ± 2°C.
3. Rinse in distilled water.
4. Etch in 100 g/liter of NaOH Solution for 1 minute at 65 ± 1°C.
5. Rinse in distilled water.

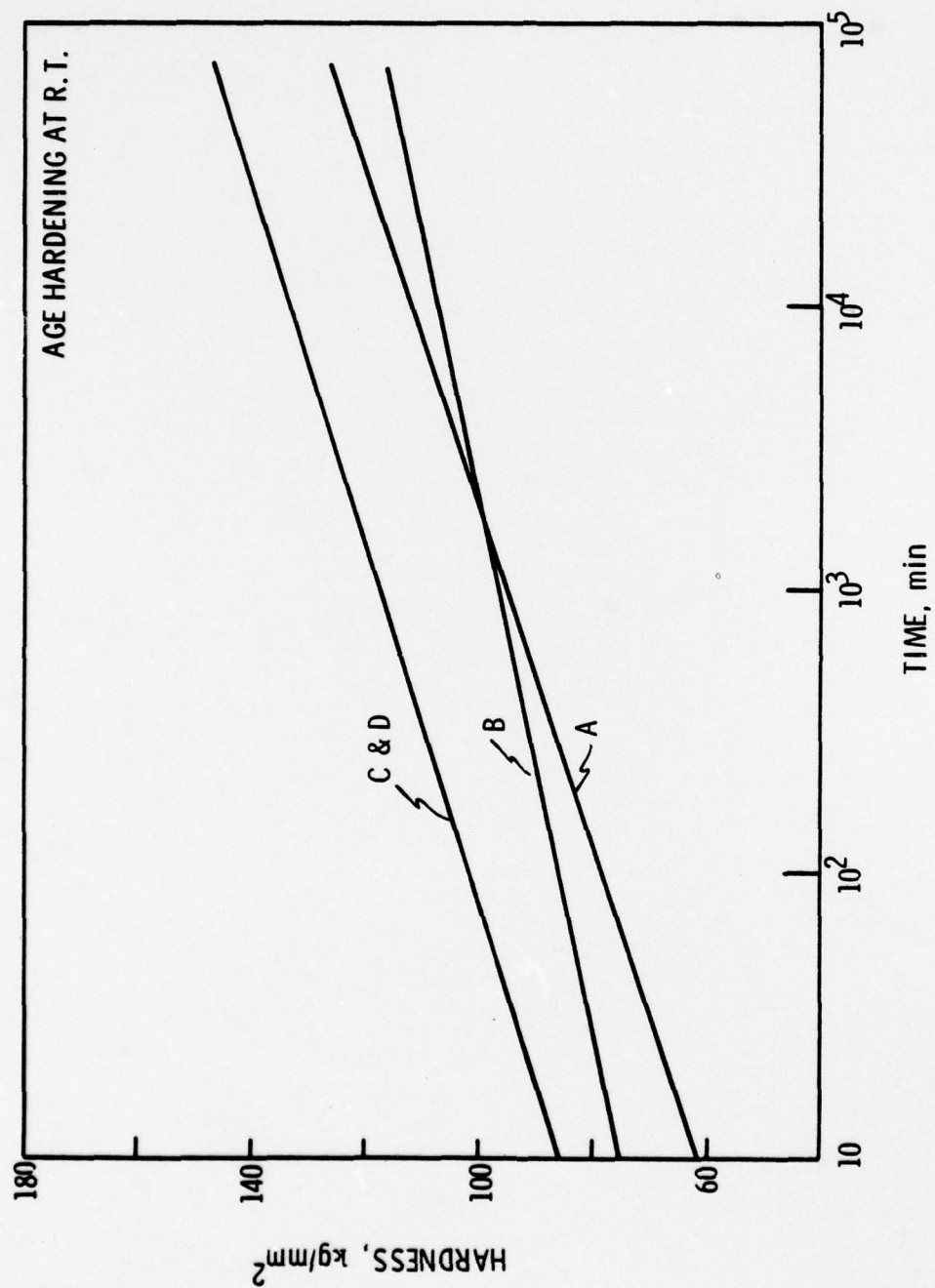


Figure 1. Age hardening curves for alloys A, B, C, and D, listed in Table I, at room temperature.

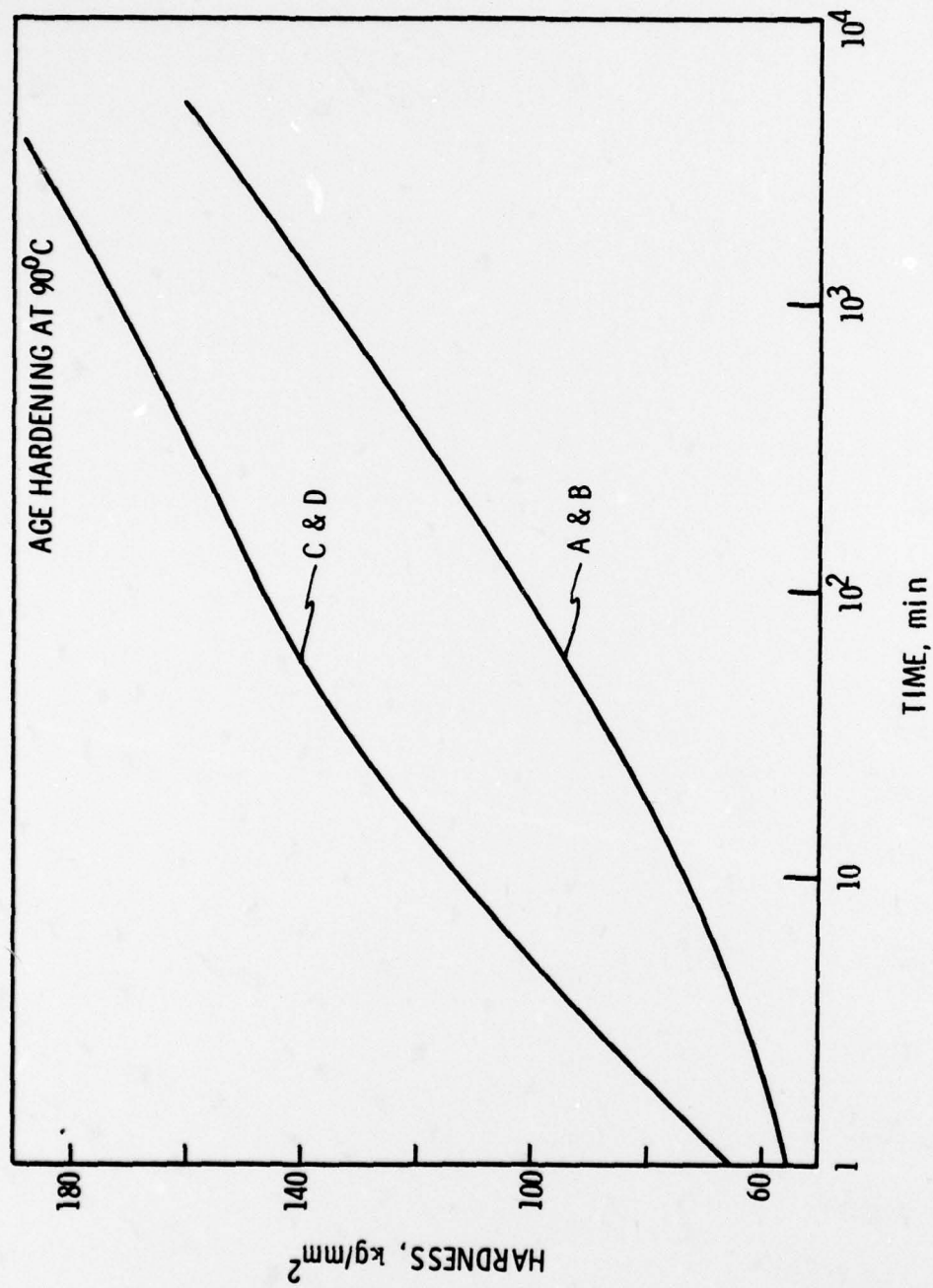


Figure 2. Age hardening curves for alloys A, B, C, and D, listed in Table I at 90°C.

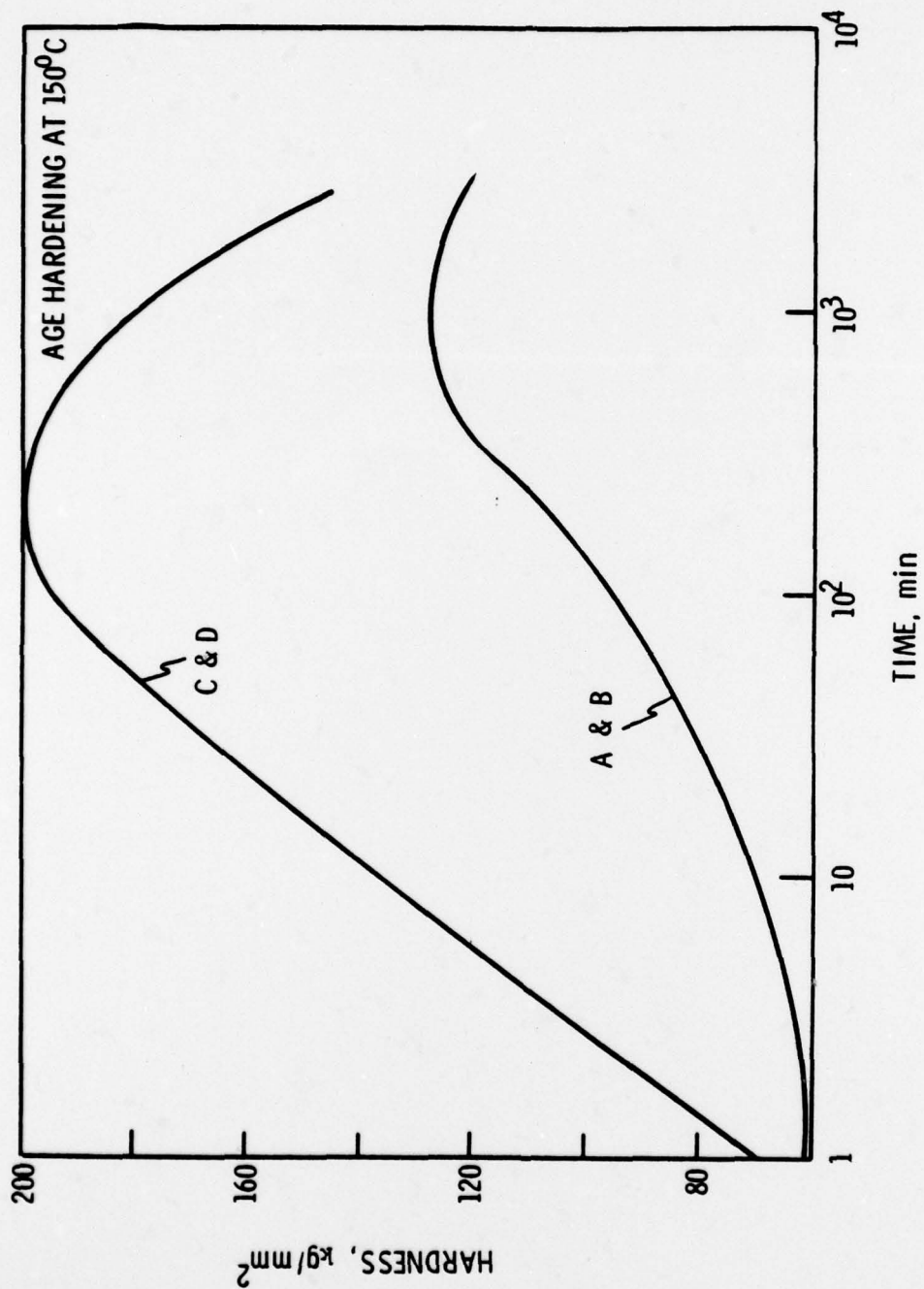


Figure 3. Age hardening curves at 150°C for alloys A, B, C, and D, listed in Table I.



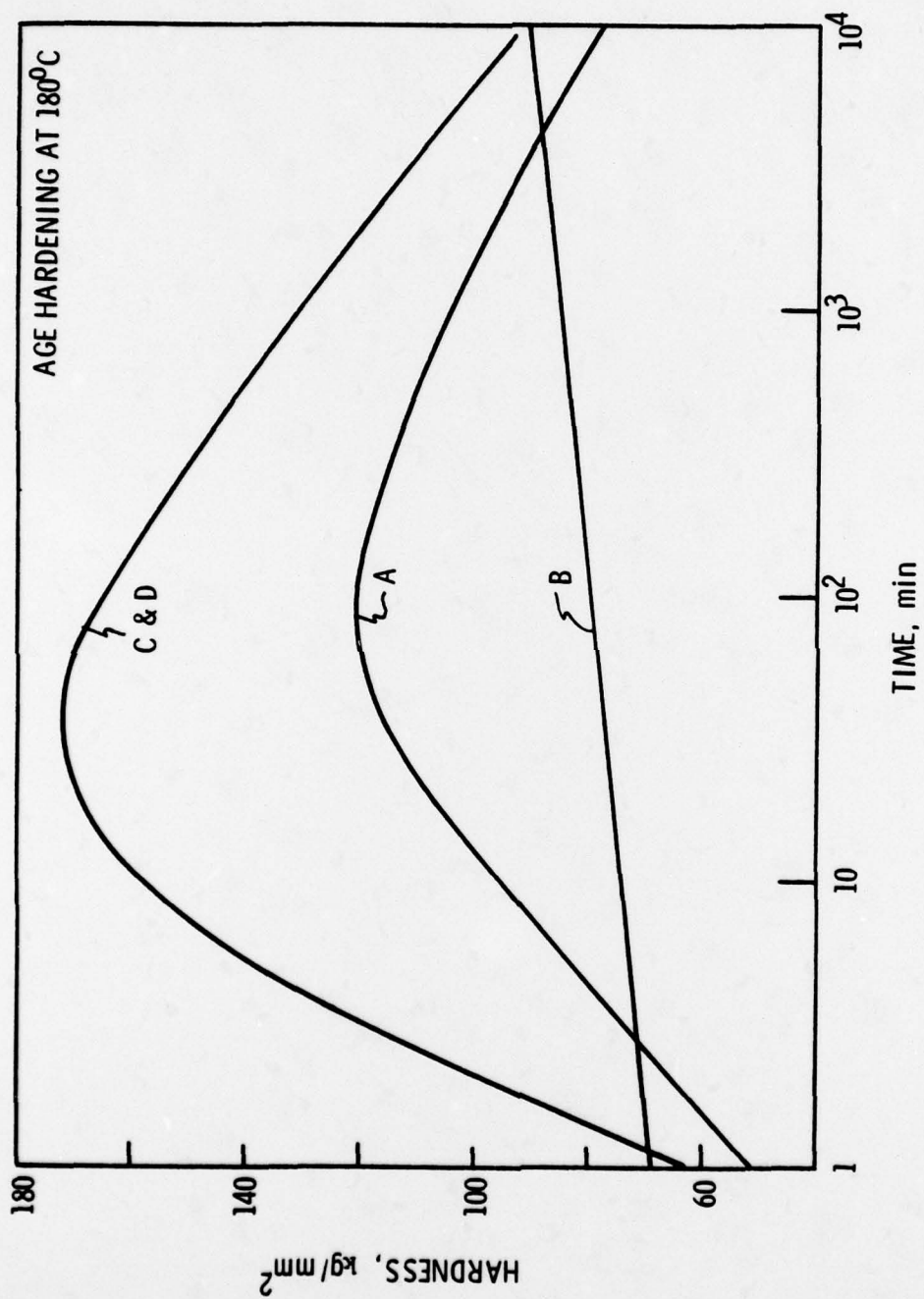


Figure 4. Age hardening curves at 180°C for alloys A, B, C, and D, listed in Table I.

6. Remove dark Zn deposit and neutralize for 1 minute in solution as in (2).
7. Rinse in distilled water.
8. Wash in acetone.
9. Dry at room temperature for 5 minutes.
10. Store in a silica gel dessicator for 24 to 48 hours.
11. Stress and place specimens in corrosive solution.

The specimens were aged at 150°C for the length of time, that, according to previously established data, should have yielded peak hardness. However, unexpected variations in yield strength and hardness resulted in systematic differences in SCC life. Fig. 5 shows the time to failure vs applied stress for alloys A, B, C, and D. The differences in SCC life between specimens A, B, C, and D may well be attributable to differences in yield strength alone. During the next program period, every effort will be made to revalidate the aging data. Sample pairs A, B and C, D will be aged to identical yield strength levels, and SCC tests will be conducted to establish the effect of the Mg/Zn ratio.

#### B. In Situ Segregation and Oxidation Studies

Quantitative information on grain boundary segregation of Al-Zn-Mg alloys in the as-quenched condition is difficult to obtain by AES studies of samples fractured in situ in the spectrometer. The principal difficulty is that the fracture surface is not totally intergranular. To resolve this issue, Ga embrittlement was used to obtain a totally intergranular fracture. However, due to selective interaction of Ga and other elements on the grain boundary, these results were not interpretable. An alternative approach is to infer grain boundary segregation features from segregation measurements on the free surface. With this aim, in situ segregation and oxidation studies were conducted on Al-Zn-Mg alloys. The results of these experiments are outlined next.

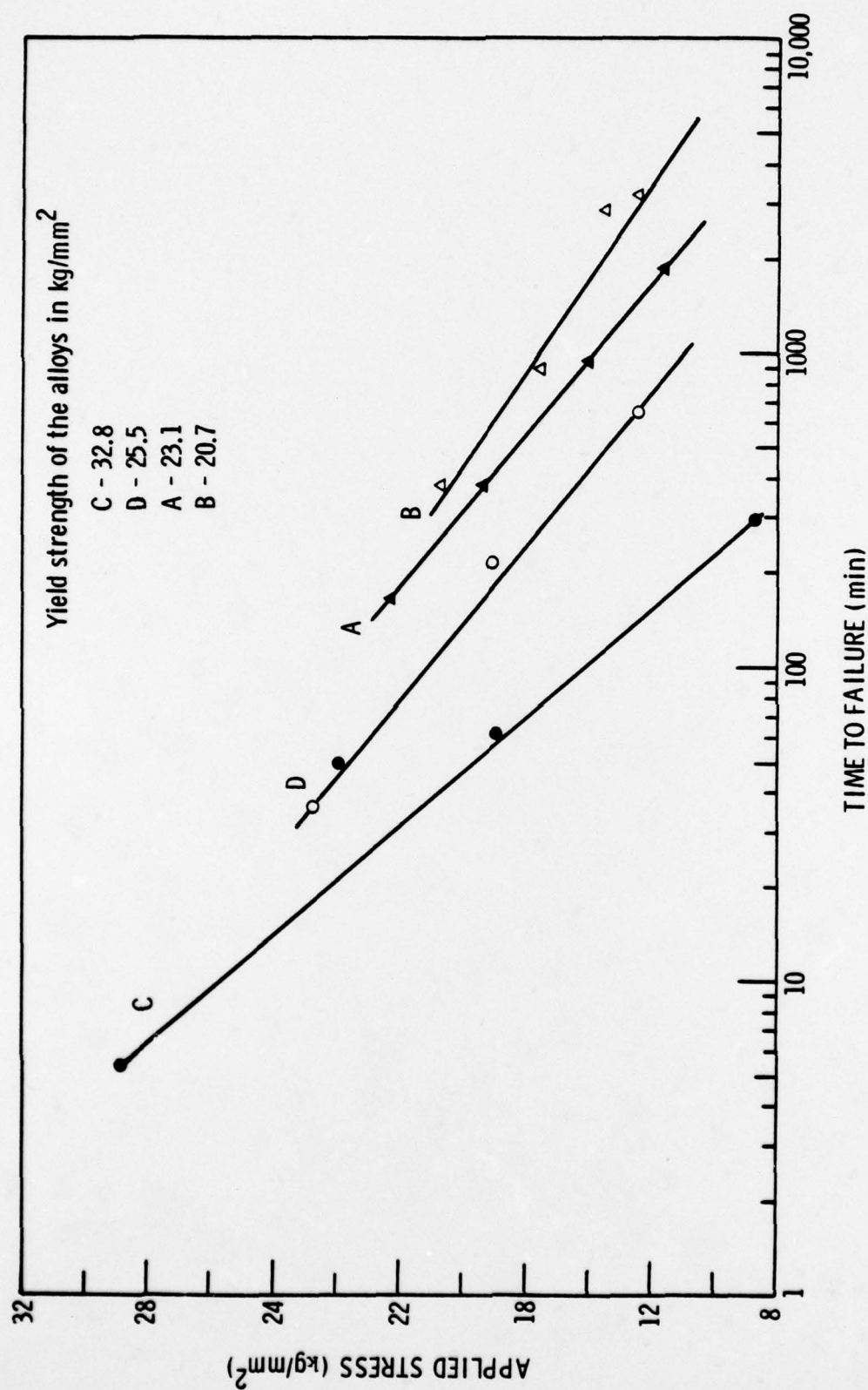


Figure 5. Time to failure vs applied stress for alloys A, B, C, and D, in constant load stress corrosion cracking tests in aqueous 3% NaCl solution at neutral pH and room temperature.



## 1. Experimental Procedure

Strips of high purity Al-5.5 Zn-2.5 Mg alloy were strain annealed to produce grains with sizes up to 1 cm x 1 cm. Specimens with different grain sizes were used to evaluate the role of grain boundaries. For large grain samples, XPS (X-ray photoelectron spectroscopy) probes an area within a grain; for small grain samples, XPS probes an area containing about 20 grains. The AES probes an area about one-fourth the size of the area probed by XPS.

Specimens with and without an initial oxide layer were used to investigate the effect of the oxide on Mg enrichment. Specimens with an oxide-free surface were obtained by Ar ion sputtering. Specimens with an oxide layer were produced in one of two ways. An air-formed oxide, about 24 Å thick, was formed by etching in a solution of 17% HNO<sub>3</sub> and 3% HF, or was formed by anodizing in a 3% ammonium tartarate acid solution to produce a 50 Å thick non-porous oxide<sup>(5)</sup>.

Heat treatments were conducted in high vacuum ( $10^{-8}$  torr of Ar) and in  $10^{-5}$  torr O<sub>2</sub> to study the interaction of O<sub>2</sub> with Mg at the surface. Heating and cooling were accomplished in situ by using two substrate geometries. In the initial set-up, temperatures up to 300°C were attainable, with heating and cooling times of about 20 to 30 mins during each cycle. Later, a smaller substrate with a temperature capability of up to 600°C was used. With this arrangement, it was possible to obtain heating rates up to 40°C/min and cooling rates up to 100°C/min by contact with a liquid nitrogen-cooled cold finger. Heat treatments were repeated either at the same temperature or at increasing temperatures to study the dependence of Mg activity on temperature and time.

## 2. Experimental Results

No surface enrichment of Mg was observed on specimens with an oxide-free surface heated in vacuum. Since thermodynamic theory



predicts surface segregation of Mg in Al-Mg alloys<sup>(6,7)</sup>, this result can only be attributed to the evaporation of Mg from the surface at a rate faster than the rate of segregation to the free surface. However, when specimens with a surface oxide were heated to 300°C in vacuum, a substantial increase of Mg was found. An Auger depth profile of this surface (Fig. 6) indicates that the maximum Mg concentration lies at the metal/oxide interface and a substantial amount of this Mg is in a metallic state.

A specimen with a 50 Å anodic oxide was heated to 300°C for 10 min, cooled to room temperature, then heated to 400°C for 10 min and quenched, and finally heated to 450°C for 5 min and quenched. XPS spectra were obtained at the end of each cycle. These spectra show that the surface Mg content increases with temperature, and the metallic component of Al appears at 400°C and increases with temperature. An Auger depth profile obtained at the end of the 450°C heating cycle shows that Mg accumulates near the metal/oxide interface (Fig. 7).

Specimens with and without an oxide layer were also subjected to a series of heat treatments in  $10^{-5}$  torr oxygen. In all cases, the oxygen was introduced after the temperature had reached the designated value and then pumped out immediately after the specimen cooled. In specimens with an oxide-free surface the reaction between Mg and  $O_2$  dominates and MgO formation is detected. Even though no surface enrichment of Mg is observed when the heat treatment is carried out in vacuum, Mg is observed in its oxide state as soon as  $O_2$  is introduced. In addition, some oxidation of Al also occurs. The Auger depth profile indicates that the maximum concentration of MgO occurs on top of the  $Al_2O_3$  layer (Fig. 8). A possible explanation is that the growth of  $Al_2O_3$  stops long before the oxidation of Mg begins to saturate.

Grain size appears to have an effect on the formation of MgO in  $O_2$  atmospheres. Small-grain samples show higher concentrations of MgO than large-grain samples, indicating a positive role for the grain boundaries in the migration of Mg during heat treatment. Also, grains of different orientation show different amounts of MgO, suggesting some

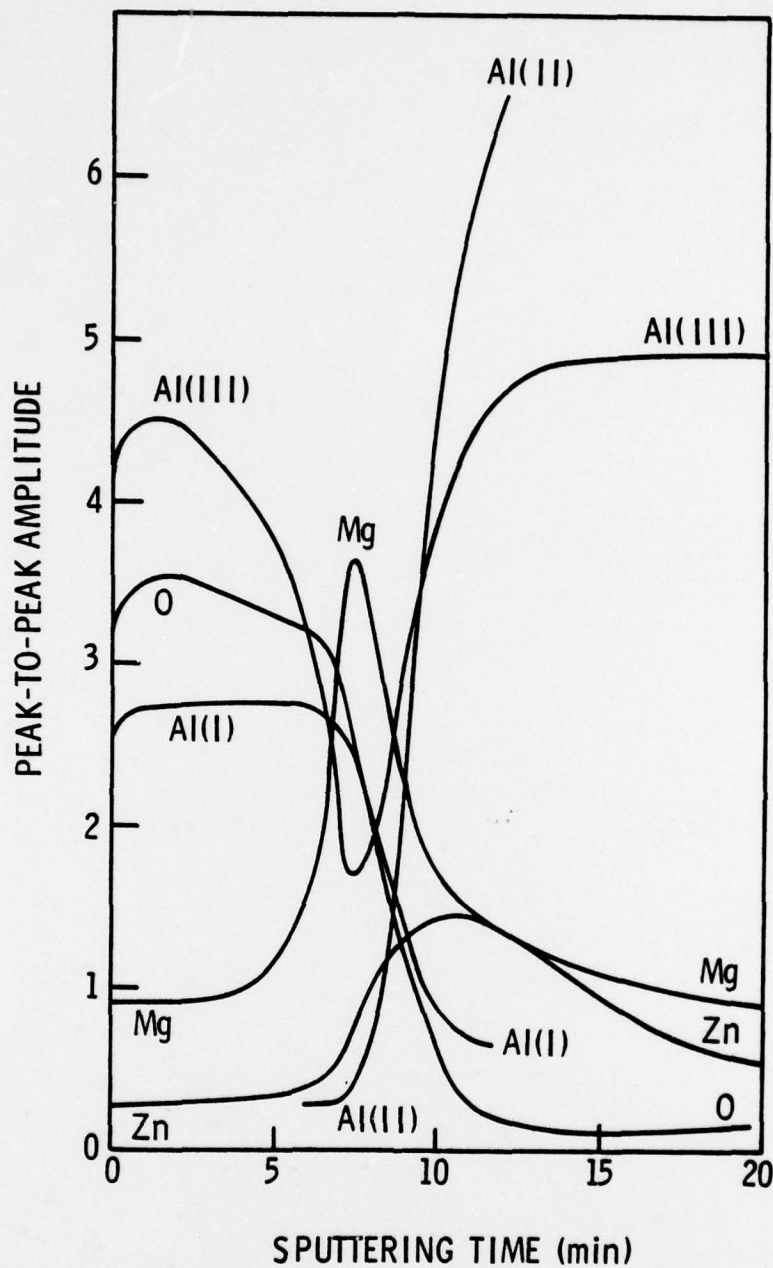


Figure 6. Auger depth profile of an Al-Zn-Mg alloy with a 100 Å anodic oxide heated to 300°C for 1 hr in vacuum. The curves marked Al(II) and Al(III) are Auger transitions at 67 eV and 1394 eV for metallic aluminum. Al(I) is an Auger transition in the oxide at 52 eV and a substantial fraction of Mg is present in the metallic state.

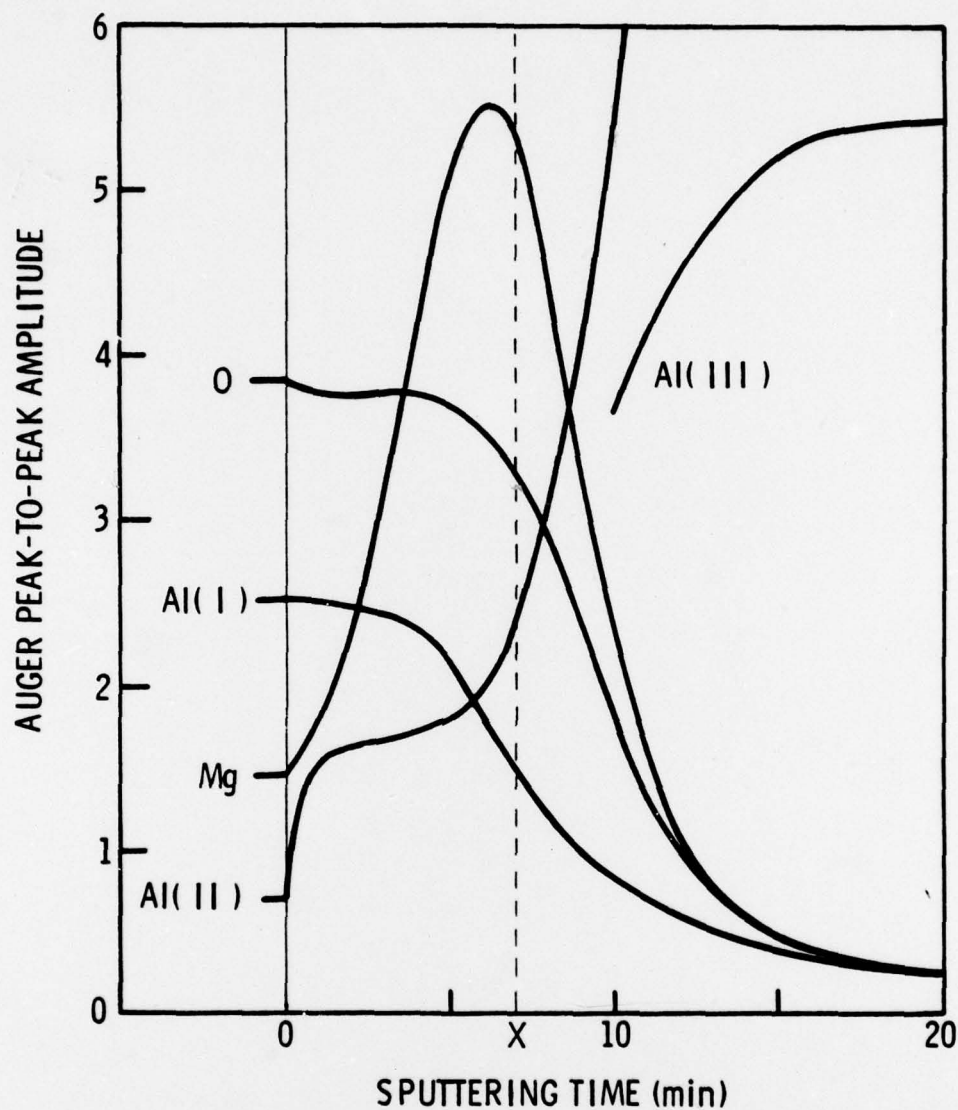


Figure 7. Auger depth profile of an Al-Mg-Zn alloy with a 50 Å anodic oxide subjected to heat treatments in vacuum. The heat treatment consisted of the following steps: a) 10 mins at 300°C and cooled, b) 10 mins at 400°C and cooled, and finally, c) 5 mins at 450°C. The AES depth profile was obtained at the end of the 450°C heat treatment. The identities of the curves are the same as those listed in Fig. 6 except that a substantial amount of Mg is now in the oxide state.

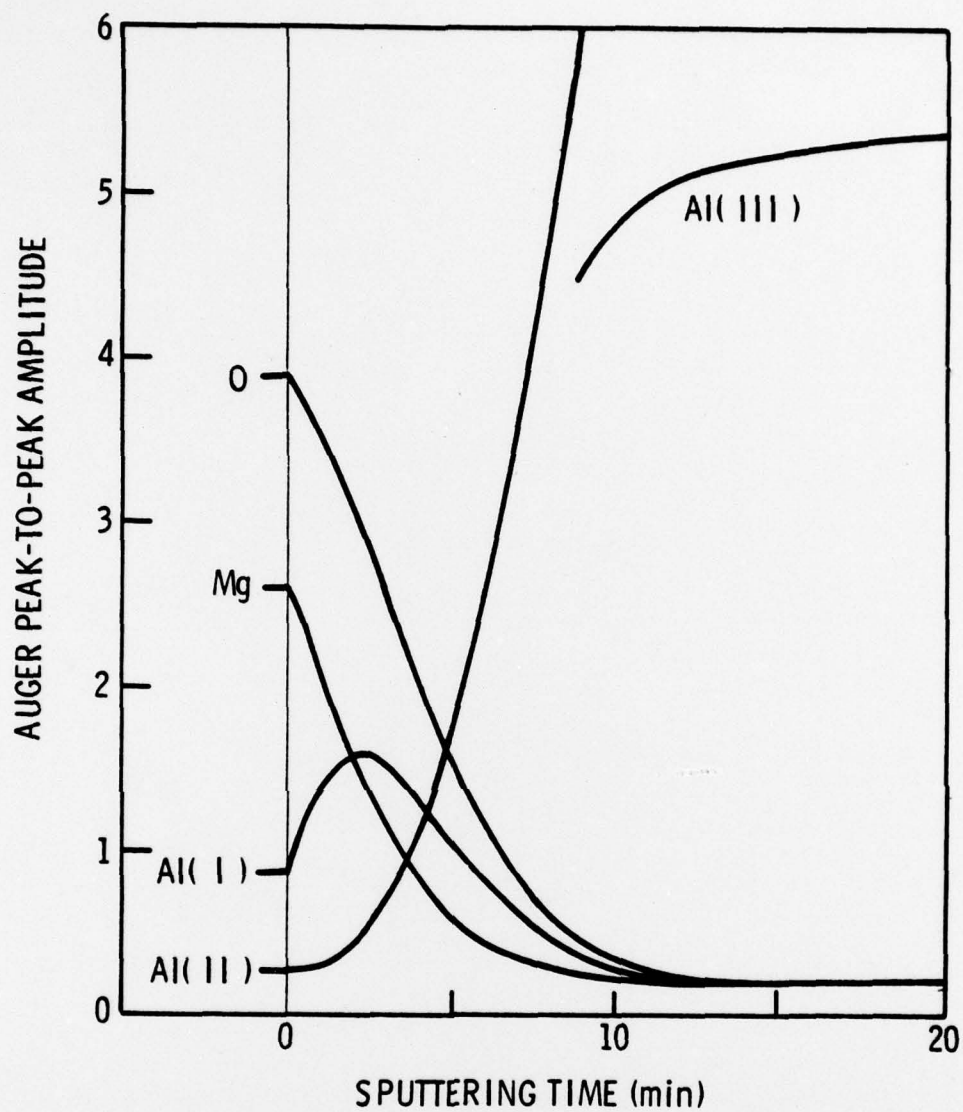


Figure 8. Auger depth profile of an Al-Mg-Zn specimen initially without an oxide film heated to 250°C in  $10^{-5}$  torr  $O_2$ . The identities of the curves are the same as those listed in Fig. 6.



anisotropy in its formation. However, if the oxide is removed and the heat treatment is repeated, the spatial differences in concentration begin to disappear, most probably due to precipitation-induced depletion in the amount of free Mg in the bulk.

Formation of MgO appears to level off after 2 hr of heat treatment at 200°C, increases sharply in the first 30 min of heating at 250°C, and begins to level off again after 90 min. This result strongly suggests that the diffusion of Mg ions in the oxide is the primary rate-limiting process in the formation of MgO, at least at low O<sub>2</sub> pressures (10<sup>-5</sup> torr).

The growth of Al<sub>2</sub>O<sub>3</sub> appears to follow a pattern similar to that for MgO, but with a significantly shorter time constant. This substantiates the previous statement that diffusion of Al ions through the oxide is associated with a higher activation energy.

In the specimen with an air-formed oxide, no detectable changes are observed except during the first hour of heat treatment, when small increases in Mg concentration and oxide thickness are observed. The AES depth profile of this specimen (Fig. 9) shows that the maximum of the Mg profile actually occurs close to the oxide/metal interface. On the basis of these findings, we conclude that an aluminum oxide layer of ~25 Å is an effective diffusion barrier for Mg at least at low O<sub>2</sub> partial pressures.

Since reduction of Al<sub>2</sub>O<sub>3</sub> by Mg ions is not important below 300°C, a significant portion of Mg is in the metallic state. High-resolution XPS spectra reveal that the metallic component dominates the total Mg concentration near the interface. However, the degree of reduction of Al<sub>2</sub>O<sub>3</sub> by Mg increases with temperature, and, at 450°C, the MgO/Al<sub>2</sub>O<sub>3</sub> ratio reaches a value close to unity.

A summary of results of these experiments is given in Table II. The composition of the oxide is expressed in terms of the total volume of MgO or Al<sub>2</sub>O<sub>3</sub> per unit area. An estimate of the total oxide thickness is also shown in the table.

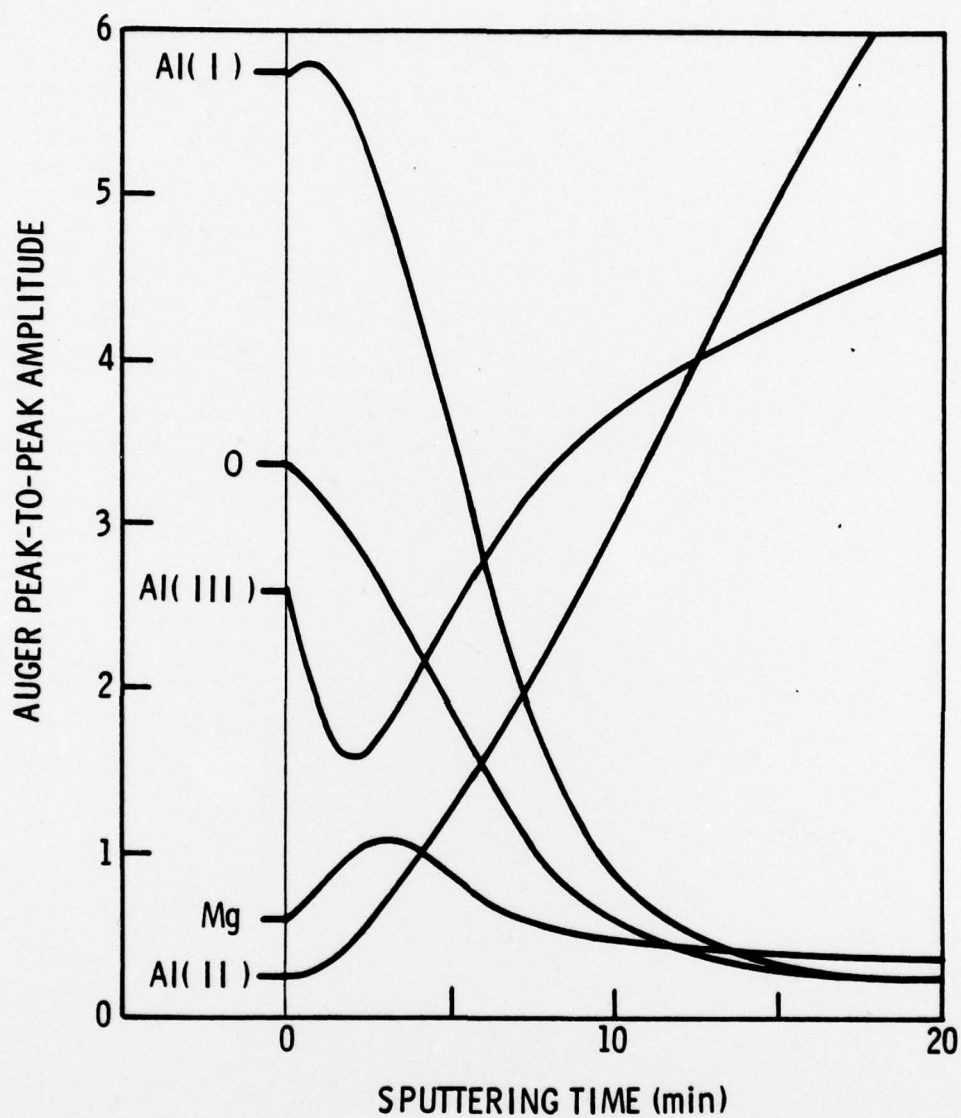


Figure 9. Auger depth profile of an Al-Mg-Zn specimen initially with an air-formed oxide heated to 250°C in  $10^{-5}$  torr  $O_2$ .

TABLE II

Surface Oxide Composition of Al-Mg-Zn Alloy Subjected to Heat Treatment in  $10^{-5}$  Torr  $O_2$ 

Heat Treatment Condition	Initial		First 1 hr @ 200°C		Second 1 hr @ 200°C		Third 1/2 hr @ 250°C		Fourth 1 hr @ 250°C	
	A	B	A	B	A	B	A	B	A	B
Specimen										
Vol. of MgO	0	0	6.0	1.6	6.4	1.6	9.1	1.6	9.9	1.6
Vol. of $Al_2O_3$	0	23.9	5.5	23.3	5.5	23.4	5.7	23.4	5.6	23.5
Total Oxide Thickness ( $\text{\AA}$ )	0	23.9	11.5	24.9	11.9	25.0	14.8	25.0	15.5	25.1

Notes: 1. Initially, specimen A has no surface oxide; specimen B has air-grown oxide.

2. Volumes of MgO and  $Al_2O_3$  are given in terms of the total volume of each species per unit area (in  $\text{\AA}$ ).



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